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THE USE OF THE ELECTROCHEMICAL PERMEATION TECHNIQUE

TO STUDY HYDROGEN TRANSPORT AND TRAPPING IN IRON

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The Use of the Electrochemical Permeation Technique to Study

Hydrogen Transport and Trapping in Iron

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The electrochemical technique has become an important tool in studying hydrogen transport in metals. In order to maximize the information obtainable, the electrochemical conditions must be carefully controlled, particularly at the input and output surfaces. Subsequent analysis of the kinetics of consecutive transients can then be used to discriminate between strong (irreversible) and weak (reversible) traps. This approach has been illustrated for iron and a number of iron-titanium alloys, and it has been shown to be possible to model the data to calculate most of the important trapping parameters in such systems.

These parameters describe trap populations that can be manipulated to control the extent of some types of hydrogen embrittlement, as illustrated by experiments on a titanium-containing HSLA steel.

The permeation technique has also been shown to be useful in detecting the occurrence and extent of dislocation transport of hydrogen in iron. Some of the implications of the effect of such a process on subsequent embrittlement in ferrous and non-ferrous alloys have been assessed.

PER LETTER

A

Introduction

Hydrogen's ability to diffuse either through the lattice or as dislocation-associated atmospheres is often directly tied to its deleterious effect on mechanical properties (1-3). This is particularly true in iron and steel where the interaction of hydrogen with localized heterogeneities is often the precursor stage to crack initiation and growth or to plasticity-controlled failure (4,5). In order to study such phenomena, a number of techniques have been developed, notably the use of the electrochemical permeation method to directly monitor the time dependence of the flux of hydrogen through a metallic membrane (6-8). The aim of this paper is to first review the methodologies, constraints, and information derivable from this technique, and to then describe how the results obtained can be used to identify or clarify hydrogen-defect interactions and their role in any subsequent embrittlement processes.

The Permeation Method

All permeation techniques have in common the measurement of the time necessary for hydrogen introduced on one surface to enter into the metal, migrate through the thickness of the specimen, and then be detected on the output side. The net integrated flux for these normally sequential processes can, in principle, be analyzed to identify the controlling kinetic factors for each of these steps. Figures 1 and 2 schematically illustrate some possible input conditions as well as suggesting two internal transport modes; lattice diffusion and dislocation transport. We will defer consideration of this latter step until later in the paper. In Fig. 1, (a) depicts the process of molecular gas adsorption, dissociation and absorption; (b) shows adsorption and absorption from hydrogen ions in aqueous solution, while (c) shows the steps for absorption after decomposition of a hydride. Since it is widely accepted that the electronic form and subsequent behavior of dissolved hydrogen is identical for all three cases, any difference in behavior found between techniques, or unaccounted differences within a given technique, must be traced to the events occuring on or near both the entering and exiting surfaces of the membrane. Because of the important kinetic role of these steps, it is necessary to consider them in some detail.

A number of studies have addressed the issue of surface control of the hydrogen entry reaction, most particularly for case (a) where gas dissociation reactions, in particular a molecular precursor step, can control .   .s (9, 10).
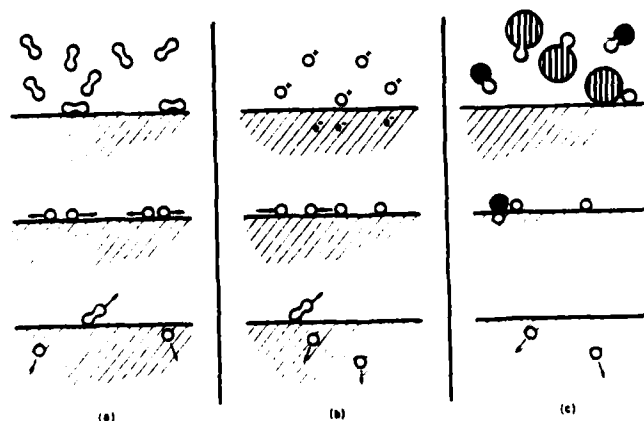

Fig. 1 Different entry steps for hydrogen

For the case of specific interest here, the electrochemical technique, the surface reactions of interest are related to the following sequence in alkaline solutions where the hydrogen gas reaction is:
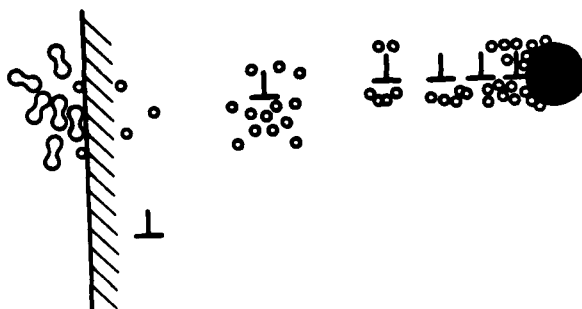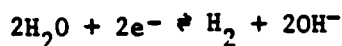
$$2H_2O + 2e^- \rightleftharpoons H_2 + 2OH^-$$

Fig. 2 Illustrative example of hydrogen transport by dislocations.

The resulting molecule may then discharge and be either:

a) physically adsorbed on the metal surface; if the molecule does not dissociate and no electron transfer occurs, this step is not important for subsequent internal diffusion.

b) chemisorbed when the bond length is extended and there is partial electron transfer. This is also relatively unimportant for internal diffusion.

c) dissociated with each atom adsorbed on the metal surface. This is a crucial step, since now hydrogen is in a form suitable for absorption and diffusion into the lattice. This step is described by the formalism MH_{ads}.

Pressouyre (11) has analyzed in detail the characteristics of this last reaction and has shown that generally, and particularly for iron in 0.1N NaOH, that the possible limiting step is where hydrogen must pass through an intermediate absorbed state on the metal substrate prior to entry. Further, he demonstrated that for the normal range of cathodic current densities used in electrochemical permeation, the coverage is Langmuirean in nature, implying low coverage and non-interacting species. He further considered the conditions under which either internal diffusion or surface reactions will control the observed flux. The comparisons were made for iron, for titanium as an alloying element in the iron, and for palladium which was often deposited on both the input and output surfaces. Palladium eliminates corrosion on the output (anodic) side, and serves as a reservoir for dissolved hydrogen on the input (cathodic) side because of its very high solubility for hydrogen. Tests for the possible importance of surface reactions for these three elements included measurements of the dependence of the permeation flux as a function of specimen thickness and input current density, as well as an examination of the shape of the curve of flux of hydrogen versus time.

Figure 3 illustrates the last of these. The experimental technique used to obtain these plots will not again be described in detail, as it is the well known application of the Devanathan and Stachurski method (6). Very briefly, a relatively thin membrane acts as a separator between two glass cells

containing, in this case, 0.1N NaOH. Galvanostatic control of the input (cathodic side) provides a constant input fugacity of hydrogen, while the output side is potentiostated, and the current necessary to maintain this constant potential is a direct measure of the hydrogen flux in the absence of all other anodic reactions. Those interested in the precise details of the technique are referred to references 6, 8, and 11.

The results shown in Fig. 3 were obtained for Ferrovac-E (purified) iron and for an alloy of iron containing 0.15% Ti. The thickness was kept constant and the membranes were studied with the input side uncoated. (The output side, for all studies, was always Pd coated) (11).
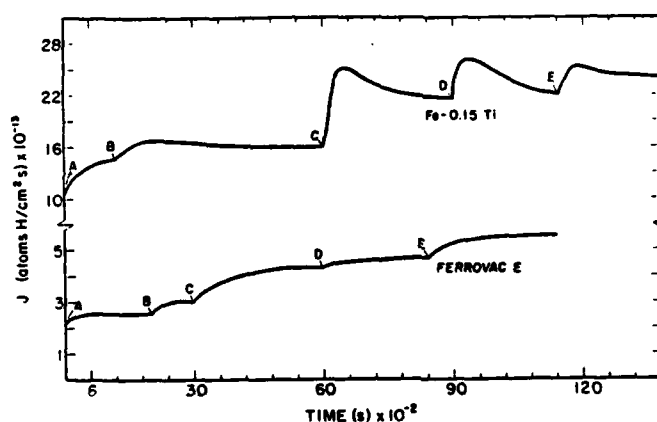

Fig. 3

Permeation transients for the two alloys with their input side uncoated. A is 2.4 mA/cm^2; B is 3.2 mA/cm^2; C is 8 mA/cm^2; D is 16 mA/cm^2 and E is 24 mA/cm^2. Reference (11).

The points, A through E, are different current densities as described. The presence of humps for Fe -0.15 Ti has been interpreted and modeled by Pressouyre and Bernstein (8) as evidence for surface trapping by Ti atoms or clusters. The alternative possibility that such maxima are caused by internal cracks and other damage generated by the hydrogen (12), has been discounted in this case since no microscopic evidence was found for such damage, and also because Fe-Ti is much less susceptible to cracking than is Ferrovac E iron, for which no hump-like behavior was found (Fig. 3) (11,13).

The effect of now plating a Pd coating on the input side for both alloys is shown in Fig. 4, with the open symbols depicting coated behavior. While a linear relationship between the steady state flux and the square root of the hydrogen concentration is obeyed for Ferrovac-E iron no matter the nature of the input surface, in Fe-Ti this is only the case when the input surface is Pd coated. Thus, in uncoated Fe-Ti, it is quite likely that entry conditions are strongly influenced by reversible surface trapping of hydrogen by titanium or irreversible surface trapping by stronger traps such as titanium carbide particles.

A final test to determine the rate controlling step for permeation is to determine the steady state flux as a function of inverse thickness. Fig. 5 shows the good fit to a linear relation found in both coated and uncoated Ferrovac-E, clear evidence for bulk diffusion being the dominant rate

controlling step in this material independent of surface treatment. In Fe-Ti this linear behavior was only found for coated specimens, a persuasive indication that the presence of Pd on a well cleaned input surface of a material containing a large number of traps is a reliable way to suppress the possible strong efforts of surface trapping on subsequent permeation behavior.
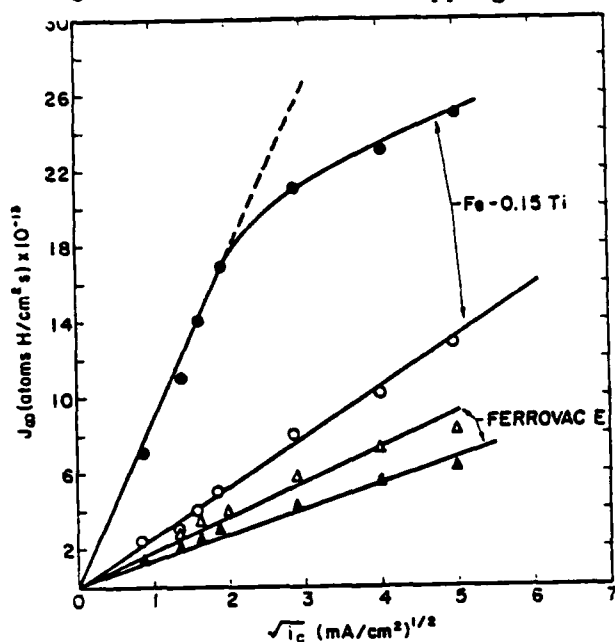

Fig. 4

Variation of the steady state flux with the square root of the current density (hydrogen concentration). Filled symbols denote that the input side is uncoated while unfilled symbols are for Pd coated input surfaces. Reference (11).
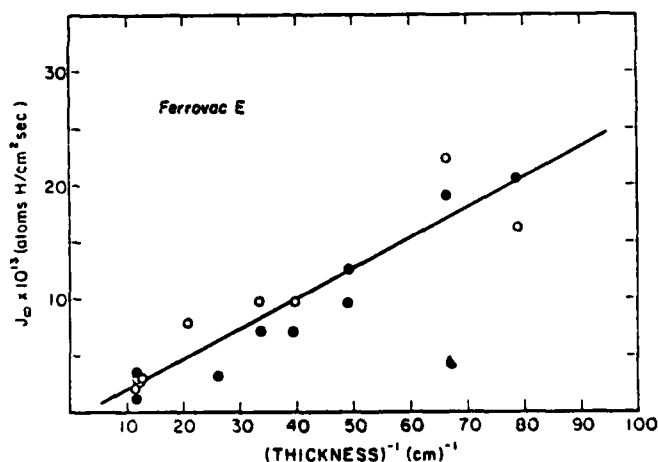

Fig. 5

Variation of the steady state flux with inverse thickness for coated (open circles) and uncoated (filled circles) Ferrovac-E. Reference (11).

In conclusion, this brief examination of the electrochemical permeation technique has considered some of the potential problems which could complicate interpretation of the kinetic data. Key requirements are to prevent extraneous anodic reaction on the output side, and to activate the input surface using a coating like Pd, which provides a ready and continuous reservoir of dissociated hydrogen ions. When these precautions are combined with control of solution chemistry and the use of sensitive electronics, the data obtained are both reliable and capable of providing detailed information on the trapping characteristics of different features in the microstructure.

Figures 6 and 7 illustrate the kinds of information that can be obtained (8,11). The first of these shows that the permeation rate can vary during repetitive polarization cycles. By performing consecutive throughput cycles, it is often observed that there are slower permeation kinetics for the first

permeation transient than for subsequent ones. This difference will often
persist into the third consecutive transients, but higher ones are invariably
identical. The second major type of result is a difference in the kinetics
of the second transient as a function of alloy content. Fig. 7 illustrates
this for purified iron and a series of Fe-Ti alloys, where the Ti is present
primarily in substitutional sites, with a small amount also present in com-
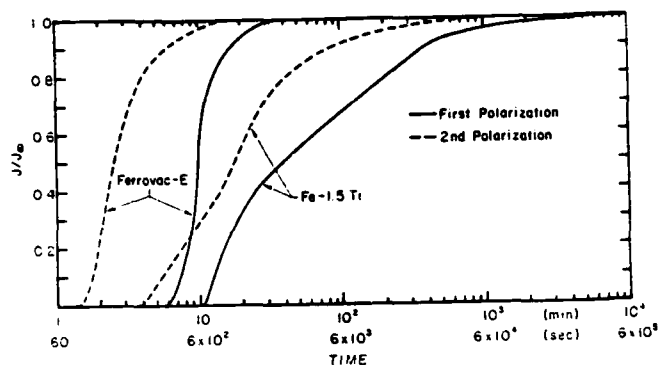bined form, mainly as TiC particles.

Fig. 6 Flux-time dependence
of the first two consecutive
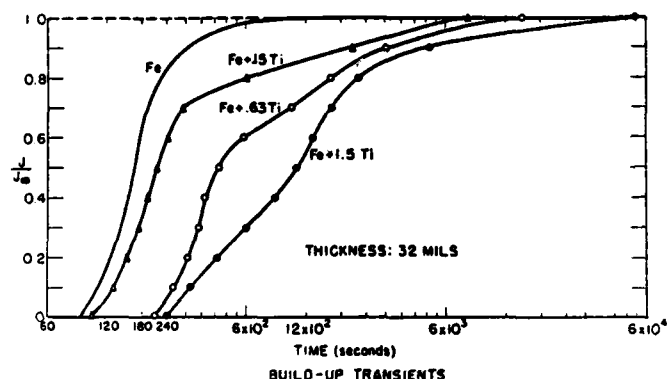permeation transients in
purified iron and Fe-0.15 Ti.

Fig. 7 Flux-time dependence
of the second permeation
transient as a function of
titanium content.

Pressouyre (1,14) has explained these observations in the following
manner: The differences between the first and second polarization are primar-
ily due to the presence of strong, irreversible traps, which become filled
during the first transient, and retain their hydrogen during the second and
higher order decay transients, thus not contributing to subsequent permeation
kinetics. The strength of such traps and their ability to affect kinetics de-
pend on such variables as temperature and the presence of specific impurities,
so that differences need not always be observed. For example, there has been
a report (15) of an inability to observe irreversible trapping in apparently
similar Fe-Ti alloys under hydrogen gas permeation conditions. Whether this
is due to differences in hydrogen fugacity between the two techniques, to a
subtle material difference, or to unknown experimental factors remains to be
determined. However, we do not subscribe to the suggestion (15) that any
observed differences between these two transients is solely due to an undes-
ignated surface phenomenon. We have seen too many cases where microstructural
control was used to vary the irreversible traps with a direct subsequent ef-
fect on permeation (1,16,17). We will shortly describe one of these in more
detail (17).

The second finding (Fig. 7) was that as the titanium content in the iron
increases, the permeation becomes slower for all transients and for all alloys.
A similar effect was found for the decay transients (8,11), supporting the un-
important role of uncontrolled surface effects in such findings. These re-
sults suggest instead that traps of varying strengths coexist in the lattices.
Since these differences now persist to higher order transients, they are likely
related to the influence of more weakly bound reversible traps, which can lose

their hydrogen during the decay transients, and thereby are capable of again
interacting with hydrogen during the next transient. The identification and
character of both types of traps have been analyzed and modeled, with the re-
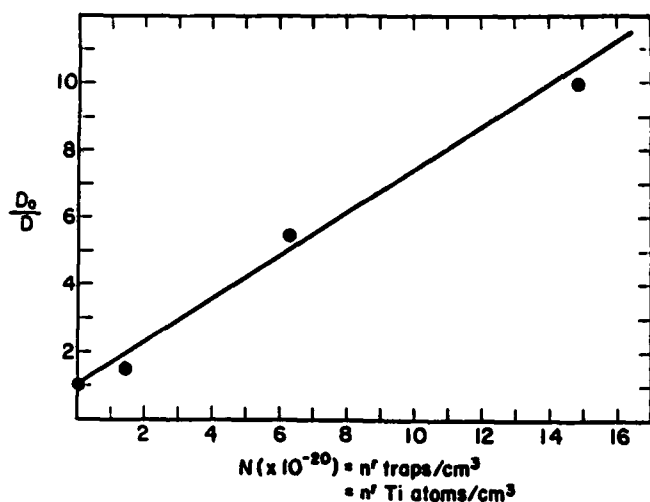sults shown in Fig. 8 & 9 (11).

Fig. 8

Experimental verification of a
linear relationship between D_o/D
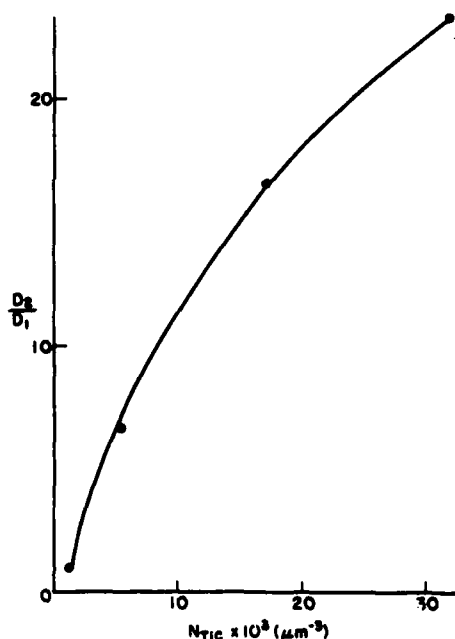and the density of Ti atoms.
Reference (11).

Fig. 9

The effect of irreversible trap-
ping by TiC particles on the
effective diffusivity. Reference
(11).

Fig. 8 is the result of an analysis extending the McNabb-Foster development
(18), in which the apparent diffusivity of hydrogen in iron containing a den-
sity of traps N_T, is related to the diffusivity in "pure" iron, D_o, by the
relationship:

$$D_o/D = 1 + \frac{k}{p} N_T \qquad [1]$$

In this model, it is assumed that D_o corresponds to a situation where no traps
exist, i.e. $N_T = 0$. This is not strictly true, of course, but the 'background'
trap density is insignificant compared, for example, to when Ti is present;
k and p are hydrogen trapping and release rate parameters defined according to
the reaction:

$$dn/dt = kC (1-n) - pn \qquad [2]$$

where: n is the fraction of traps occupied at time, t; and C is that hydrogen concentration which can diffuse and is thus capable of undergoing a trapping reaction. Equation [1] further assumes that the traps are sparingly occupied; in the particular case of trapping of hydrogen by titanium solute atoms, this has been shown from solubility measurements and calculations to be the case (8).

Taking for D_o the experimental value found for Ferrovac E, (D_o = 6.1 x $10^{-6}cm^2/s$), (11), the ratio D_o/D is plotted in Fig. 8 as a function of the experimentally known numbers of titanium traps which, for the particular non-carburized alloys used, is close to the total titanium content of these alloys. A linear relationship is obeyed, supporting the assumption that titanium atoms are the reversible traps responsible for the decrease in diffusivity during second polarization transients for the four alloys examined.

Further information on the trapping characteristics of titanium atoms was obtained; in particular, from the slope of Fig. 8 a value for the ratio of the trapping rate parameters was calculated (8):

$$1 \times 10^{-21} < k/p < 6.3 \times 10^{-21}.$$

Pressouyre and Bernstein (8,11) chose alloys where the three parameters, D_o, the input hydrogen concentration, and the precise number of reversible traps, were all known, which permitted both k and p to be calculated. The average values, quite independent of titanium content, were found to be: p = 1 x 10^{-3} s^{-1}; and 1.1 x 10^{-24} < k < 7 x $10^{-24} cm^3/at\cdot s$, with the range due to considering that from one to six equivalent octahedral sites about a Ti atom are available for trapping.

They further studied the effects on permeation kinetics of carburizing the alloys of Fig. 8 with from 320 to 650 ppm total C. Assuming reaction kinetics sufficient to form the equilibrium amount of TiC (as verified by quantitative metallography), the effect of irreversible TiC hydrogen traps on the first permeation transients was measured and analyzed (8). Fig. 9 compares the diffusivity of carbide-free titanium alloys (D_1) to those containing carbides (D_2), for equivalent number of reversible traps. As expected, this ratio increases with carbide density, supporting the premise that TiC particles can provide strong trapping sites for hydrogen, at least at room temperature.

Effect of Traps on Mechanical Properties

The role of such traps on mechanical behavior and permeation was more systematically studied in an experimental high purity HSLA steel, containing 0.064 C, 1.37 Mn, 0.22 Ti, 0.26 Si, 0.003 P and 0.007 S (17). In this alloy, the TiC morphology and size were controlled by solutionizing at 1200°C, quenching in iced brine, and subsequent aging for 1 hr. at temperatures up to 900°C. The resultant microstructures, for aging temperatures up to 700°C, consisted of acicular ferrite with spheroidal carbides, as illustrated in dark field transmission electron micrographs of Fig. 10. For carbide sizes between 30-150Å, the TiC particles begin to lose coherencey with the concurrent formation of interfacial dislocations; above 200Å, it is reported that they become incoherent (19). For aging temperatures below about 700°C, the strength is nominally constant, allowing the direct effect of internal hydrogen on the reduction of area to be studied at constant strength level; any changes observed must then be attributable to the changing nature of the TiC particles. The results of such tests are shown in Fig. 11. The Figure also shows that in the

uncharged condition, aging has only a modest effect on subsequent ductility.

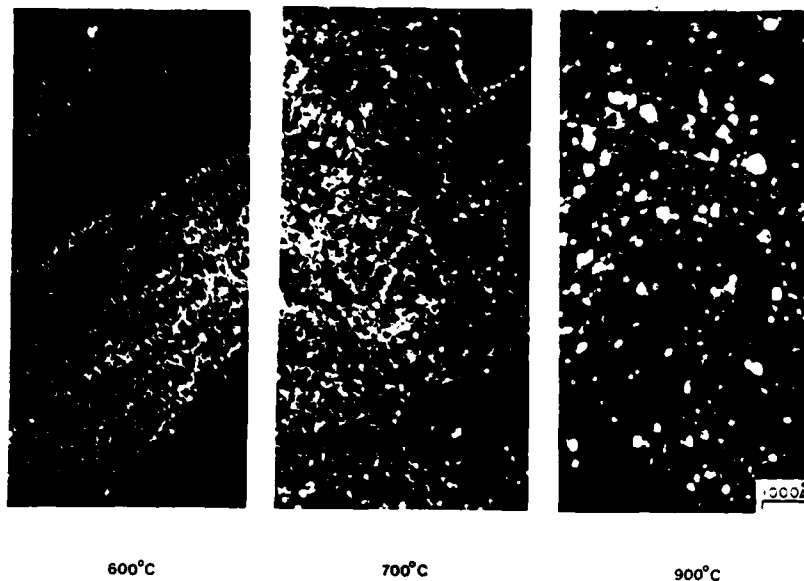600°C   700°C   900°C

Fig. 10

TEM dark field micrographs of carbide distributions and
sizes at aging temperatures of 600, 700 and 900°C. Ref. (17).

The small dip at 600°C may suggest a predisposition for temper embrittlement,
perhaps due to the presence of Si segregation. The results shown in this Figure
illustrate two important conclusions: Changing the nature of the carbide af-
fects the extent of embrittlement for most hydrogen contents, and this bene-
ficial effect is lost at higher hydrogen contents, presumably when the traps
become saturated. The role of these traps can be better appreciated by com-
paring the effective hydrogen diffusivities calculated from the first and
second permeation transients for different heat treatments, as illustrated in
Figure 12 (17). The largest difference between the two, found for the 600°C
age, must be due to the presence of strong, irreversible TiC traps which be-
come filled during the first transient and thus do not affect subsequent hy-
drogen permeations. To summarize the tensile results, the presence of irre-
versible traps in this steel reduces the tensile RA loss, presumably because
the hydrogen is now innocuously trapped. When such traps are filled, for ex-
ample by increasing the initial hydrogen content, this beneficial effect is
lost.

These results also clearly show that one can use differences between con-
secutive transients to discriminate between different trap types. There ap-
pears to be no other way to interpret the results of Fig. 12, since the only
significant microstructural change with low temperature aging is a varying
degree of coherency of the TiC particles. Thus, the large changes observed
in the apparent diffusivity, calculated from the first and second polariza-
tions, cannot be seriously ascribed to unaccounted surface trapping. To re-
iterate this position in the more general context of information derivable
from electrochemical permeation transient measurements, surface trapping and
other reactions can occur, but they can be both accounted for and usually
eliminated by plating with a material like palladium on both the input and
output surfaces.

The final topic to be covered is the use of permeation transients to
detect and measure the extent, if any, of enhanced transport of hydrogen by

mobile dislocations generated during concomitant plastic deformation. This
process was schematically illustrated in Fig. 2. The major advartages of the
electrochemical technique for doing this is the ease of generating the large
input fugacities needed for materials with either low solubilities or lattice
diffusivities, like nickel and aluminum, and also because the input fugacity
can be rapidly varied. Gas phase permeation procedures could be as effective
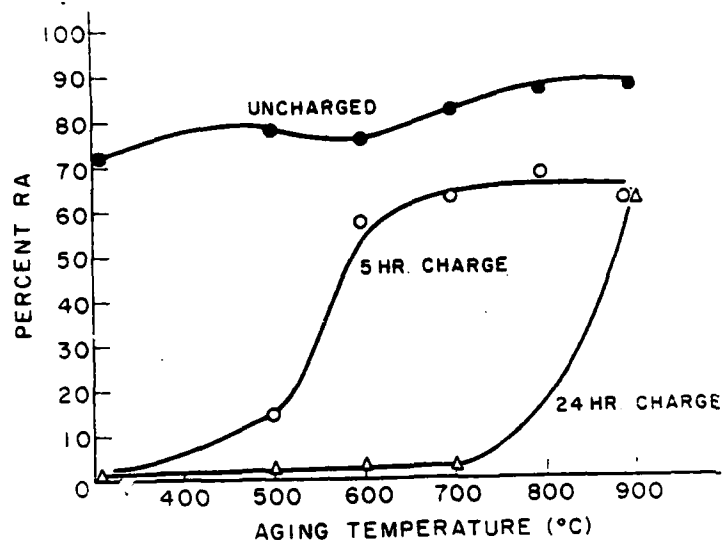in many cases however.

Fig. 11

Effect of carbide morphology
on tensile ductility at two
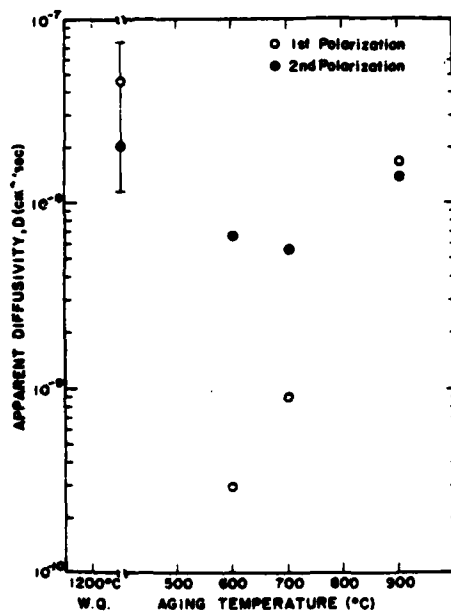bulk hydrogen concentrations.
Reference (17).

Fig. 12

Diffusivity ratio as a function of
ageing temperature for the first and
second permeation transients. Refer-
ence (17).

Tien et.al. (20), following earlier work (21), have examined the poten-
tial implications of hydrogen interacting with mobile dislocations, and in
particular whether this can lead to enhanced concentrations of hydrogen in the
bulk in excess of that predicted from thermodynamic equilibrium considera-
tions.

Although the significance of these effects have been questioned (22-24), particularly the importance of transient effects on local concentration enhancements (24), much of this disagreement has now been resolved (24,25), and the current status of this phenomenon has, in our opinion, been clearly elucidated in the recent paper by Nair, Jensen and Tien (26). The importance of their analysis is that they have modeled situations where internal traps can interact with the hydrogen-containing dislocations. They found that when either reversible or irreversible unsaturated traps are present, significant enrichment at the boundaries of these traps is possible by stripping of hydrogen from dislocations, both for high and low lattice diffusivity materials. Specifically, conditions and materials where trap strengths vary from 0.4 ev/atom to 1 ev/atom, and lattice diffusivities from $10^{-6}cm^2/s$ to 10^{-10} cm^2/s can all exhibit both dislocation transport and local enrichment of hydrogen for particular and predictable temperatures and strain rate regions. One particularly interesting implication of this is, if the transient period of enrichment is long enough compared to say, a tensile, or fracture mechanics test, so that high local concentrations of hydrogen could form at those defects which could be potential crack or ductile failure initiators, hydrogen embrittlement could be accelerated. Indirect evidence for such a scenario has been found for a spheroidized steel (27), and more directly for a high strength aluminum alloy (28), with the latter results to be discussed shortly.

Experimental verification for dislocation transport of hydrogen has been reported in nickel by Kurkela and Latanision (29), who found enhancement of the apparent diffusivity by up to five orders of magnitude. A recent suggestion that these effects were due to Joule heating associated with the high fugacities and current densities needed to observe measurable permeation rates (30) is not convincing (31), and it is our opinion that this direct result, as well as other indirect measurements, provide clear proof of the existence of hydrogen transport.

Because of both its technical importance, and the useful experimental variables of intrinsically high diffusivity and good control of electrochemical reactions on the output side of a membrane, it is of interest to ascertain whether such diffusivity enhancements can also be detected in iron and iron alloys. Some current work on steels suggest only enhanced trapping during plastic deformation (31,32) with the effective diffusivity thus actually decreasing. We have chosen to focus our studies on purified iron, where intrinsic trapping densities are much lower, and where slip lengths should be longer than in commercial steels. Preliminary results from these studies in progress are given in Figures 13 and 14 (33).

The schematic of Fig. 13 shows the kind of behavior that can be observed. Region I is the steady state flux for annealed Ferrovac-E iron. The imposition of an elastic stress (region II), causes a small increase in flux which could be due to either, or both, surface effects and a small tensile-induced increase in the solubility. The onset of significant plasticity leads to a reduction in the steady state flux (region III) at first, as observed by others (31,32). However, with further straining, the flux begins to increase steadily. We have interpreted region III as one where trapping by the newly created dislocation density is increasing rapidly. At higher strains, enhanced transport begins to dominate as the rate of production of dislocations slow. Upon now reducing the strain-rate to zero, the flux at first remains constant as strain relaxation continues to move dislocations through the output surface (region IV). The subsequent increase in flux is believed due to the reversible dislocation traps now releasing their hydrogen. Although speculative, these interpretations are self-consistent and support the occurrence of enhanced transport of dislocations by hydrogen in iron. Further, by comparing the effective diffusivities in regions III and IV, an enhancement factor can

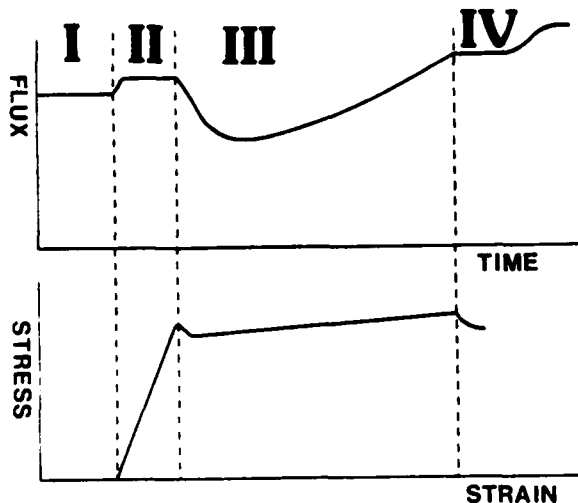be obtained at an effectively constant cold-worked structure (33).

Fig. 13

Changes in the steady state permeation flux from the unstrained state due to concurrent plastic deformation.
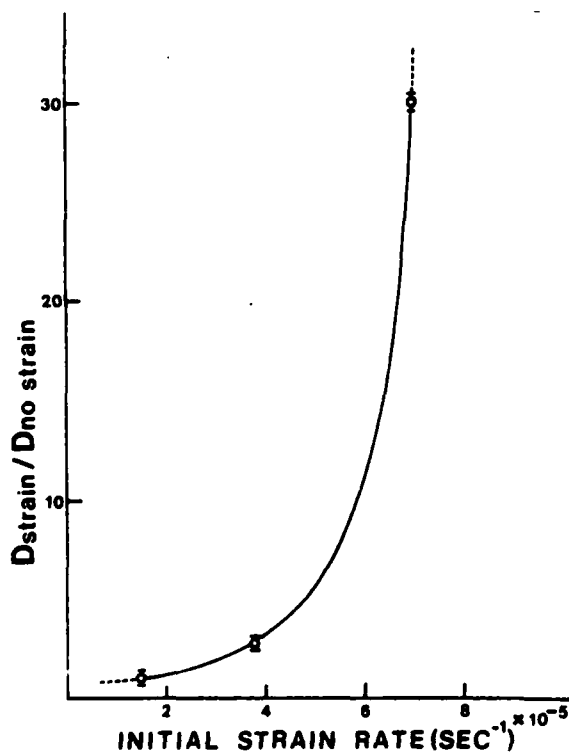

Fig. 14

Strain rate dependence of the diffusivity ratio with and without concurrent plastic deformation.

Fig. 14 shows that large enhancements are possible due to plastic flow, with the ratio increasing with increasing strain rate, as predicted (20,24). We did not find a critical velocity (strain rate) for a breakaway, but it is probable that in iron, this is several orders of magnitude greater than the strain rate range employed (20,24).

What of the possible effects of dislocation transport on hydrogen embrittlement? We have not yet determined conclusively if it can play a significant role in iron, although there are suggestive implications for this (27). However, we do have evidence that it can be quite important in aluminum (28), as illustrated by the results shown in Fig. 15. A high purity heat of the high strength aluminum alloy 7075 containing in wt. pct. 5.6 Zn, 2.52 Mg, 1.55 Cr, 0.02 Si, 0.01 Mn and 0.03 Ti was tested in the underaged condition where the

strengthening particles can be cut or sheared upon deformation, promoting planar slip. In the uncharged condition, tensile tests led to a completely ductile failure mode with a considerable strain to fracture. When cathodically charged, the uniform strain and reduction in area were reduced by as much as 40% and a brittle surface intergranular zone one or two grains deep was formed; the remainder of the fracture face was largely microvoid coalescense. But when specimens were simultaneously strained at a very low strain rate during cathodic charging, the intergranular zone widened to include almost the entire specimen diameter (28). Since tests were performed under electrochemical conditions where passive surface films should not form, and since reversibility of the effect was established by outgassing with a return to initial properties, and since the severity of the effect was a function of strain rate, we are convinced that these results clearly show that hydrogen discharged at the surface can be carried deeply into the specimen interior by mobile dislocations, leading to a large enough grain boundary concentration of hydrogen to then promote premature intergranular failure.

UNCHARGED

CHARGED

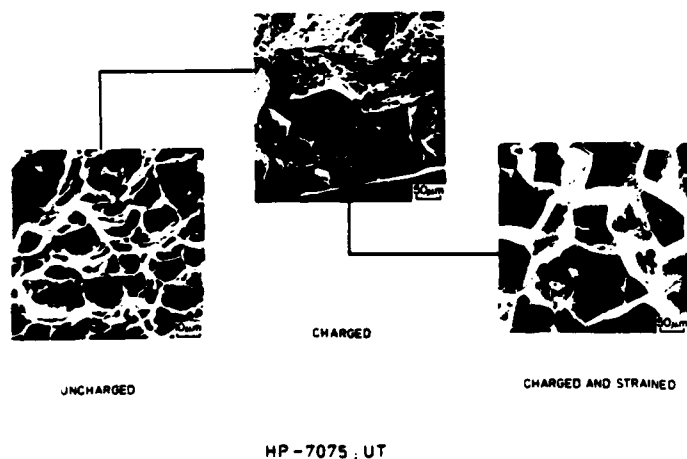CHARGED AND STRAINED

HP-7075 UT

Fig. 15

Fractography of equiaxed HP-7075 in the underaged condition. Static charging shows one or two grains of intergranular fracture while simultaneous straining leads to almost all intergranular fracture. The normal fracture mode is microvoid coalescence.

Conclusions

The important techniques necessary to make optimum use of the electrochemical permeation method in order to study hydrogen transport and trapping have been reviewed. It is critically important that the behavior at both the input and output surfaces are known and controllable in order to be able to separate out surface effects from internal transport behavior. The best way to date to do this is to deposit palladium on both surfaces, and to then check for the possible occurrence of surface trapping by monitoring the thickness and concentration dependence of the steady state flux. This is not difficult to do, and, at least in iron and its alloys, results can be easily obtained and modeled to provide qualitative and quantitative information on the type, number and strength of reversible and irreversible traps, both at the surface and in the bulk. Such types of characterization studies permit predictions of the optimum kinds of microstructures (5,34) expected to show enhanced resistance to hydrogen embrittlement, under conditions where the hydrogen is present as an external environment or where the hydrogen is dissolved in the material prior to the application of a stress. In both cases, dislocation transport is anticipated to serve as a way to rapidly redistribute hydrogen to local failure centers, often increasing the extent of the observed embrittlement. Environmental fracture remains an area replete with incomplete information, with detailed experimental studies and mechanistic fundamentals needed. We believe that intelligent use of permeation results, obtained by the electrochemical or gaseous technique (8,15) will provide needed information to improve our

understanding of this complex phenomenon.

Acknowledgements

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20. ABSTRACT *(Continue on reverse side if necessary and identify by block number)*
The electrochemical technique has become an important tool in studying hydrogen transport in metals. In order to maximize the information obtainable, the electrochemical conditions must be carefully controlled, particularly at the input and output surfaces. Subsequent analysis of the kinetics of consecutive transients can then be used to discriminate between strong (irreversible) and weak (reversible) traps. This approach has been illustrated for iron and a number of iron-titanium alloys, and it has been shown to be possible to model the data to calculate most of the important trapping parameters in such

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systems.

These parameters describe trap populations that can be manipulated to control the extent of some types of hydrogen embrittlement, as illustrated by experiments on a titanium-containing HSLA steel.

The permeation technique has also been shown to be useful in detecting the occurrence and extent of dislocation transport of hydrogen in iron. Some of the implications of the effect of such a process on subsequent embrittlement in ferrous and non-ferrous alloys have been assessed.

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